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BRILLOUIN SCATTERING STUDIES OF THE GLASS TRANSITION OF ORIENTE--ETC(U)

FEB 82 R J ADAMIC, C H WANG

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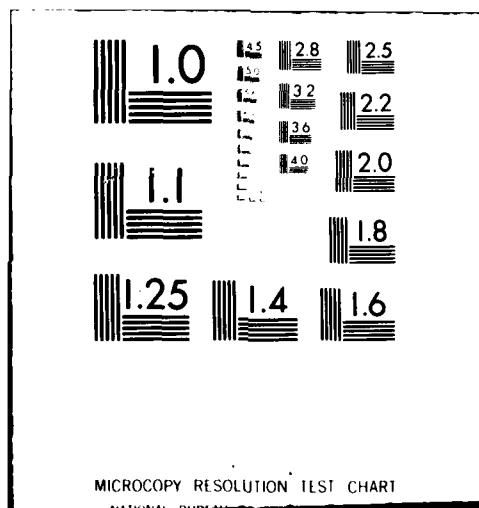
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stretch ratio, whereas the high glass temperature  $T_g$  remains unchanged. Between  $T_{g1}$  and  $T_{g2}$ , the hypersonic velocity  $g_2$  decreases in magnitude.

Analysis of the velocity data shows that the glass transition has a most pronounced effect on  $C_{33}$ . Significant disagreement is found between the ultrasonic and Brillouin scattering data. Theoretical calculations using the recently developed orientation model by Wang show good agreement with the Brillouin data. The Voigt model of Ward gives a result slightly lower than the experimental values in both  $C_{11}$  and  $C_{33}$ .



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Brillouin Scattering Studies of the Glass Transition  
of Oriented Semicrystalline Polypropylene Films

By

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Brillouin Scattering Studies of the Glass Transition of  
Oriented Semicrystalline Polypropylene Films

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### Abstract

The quasi-longitudinal and quasi-transverse hypersonic velocities are determined using Brillouin scattering for the isotactic polypropylene (PP) films as a function of stretch ratio at various temperatures (ranging from 190 to 330 K) with a particular emphasis on the glass transition region. The study shows that the glass transition in the PP film is reflected by a spread of the glass transition temperatures bordered by  $T_{g_1}$  and  $T_{g_2}$ . The lower glass temperature  $T_{g_1}$  decreases with increasing stretch ratio, whereas the high glass temperature  $T_{g_2}$  remains unchanged. Between  $T_{g_1}$  and  $T_{g_2}$ , the hypersonic velocity decreases in magnitude. Analysis of the velocity data shows that the glass transition has a most pronounced effect on  $C_{33}$ . Significant disagreement is found between the ultrasonic and Brillouin scattering data. Theoretical calculations using the recently developed orientation model by Wang show good agreement with the Brillouin data. The Voigt model of Ward gives a result slightly lower than the experimental values in both  $C_{11}$  and  $C_{33}$ .

## Introduction

The behavior of a polymer at the temperature of the glass transition,  $T_g$ , is frequently studied by examining changes in the mechanical properties of the polymer as a function of temperature. Mechanical properties such as the linear thermal expansion, sound velocity, and elastic modulus show either smooth, gradual changes or sharp, discontinuous breaks near the glass transition region. The glass transition is understood not a thermodynamic phase change; rather it is a kinetic effect where the relaxation time of some dynamic property of the polymer changes as the temperature (or pressure) changes.<sup>1</sup> Microscopically, the glass transition temperature reflects the point at which the long range motions of the polymer chain become frozen in, and only short range, local motions are allowed. In completely amorphous polymers, the freezing-in of the polymer chain backbone represents a primary relaxation process and is designated as  $T_g$ . Secondary relaxations may also occur below  $T_g$  when the amorphous polymer is in the glassy state, and the relaxations result from short range, usually side group motions of the polymer. However, with partially crystalline polymers where both amorphous and crystalline phases are present, assignment of primary and secondary relaxation processes becomes more difficult. In two phase polymer systems the polymer may have relaxation processes in both phases.

There is an unanimous agreement in the literature that polypropylene is a two phase solid. Isotactic, syndiotactic and atactic forms of polypropylene can be obtained using different polymerization techniques. The isotactic and syndiotactic forms are semicrystalline,<sup>2</sup> and the atactic polymer is amorphous. Polycrystalline polypropylene solid consists of crystalline fibrils forming some type of spherulite, with the atactic molecules lying trapped between crystalline fibrils.<sup>3</sup>

Commercial isotactic polypropylene (PP) consists of isotactic chains for the most part and includes only a minor fraction of atactic and stereoblock chains.

Comprehensive mechanical studies at low frequency have been made by Flucke<sup>4</sup> and Passaglia and Martin.<sup>5</sup> The morphology of isotactic PP solids has also been studied by Wada et al.<sup>6</sup> Measurements of linear thermal expansion and shear modulus and dielectric loss as a function of temperature have revealed several relaxations. The dominant one is termed as the  $\beta$  relaxation. This relaxation is now understood as the glass-rubber relaxation of the amorphous portion of the solid.<sup>2,7</sup> The amorphous phase includes atactic as well as isotactic chains, and consequently the nature of the amorphous phase varies with the ratio of the two kinds of chains. The reported temperature in the literature for the  $\beta$ -relaxation in semicrystalline PP is between 250-260K.<sup>7</sup>

The study of orientation on partially crystalline polymers is important to understanding their physical properties. Orientation can be considered as a convenient variable, which alters the mechanical properties of the polymer and, therefore, permits useful information to be acquired. It has been shown that when polypropylene is uniaxially stretched or extruded, the direction for sound propagation is increased along the stretch direction.<sup>8</sup> This has been revealed by the increase in the elastic (stiffness) constant along the stretch direction as the draw ratio increases. In contrast, the elastic moduli for directions orthogonal to the orientation direction show no increase in magnitude, and in some instances show a decrease as a function of draw ratio.

In this paper, we report the results of investigating semicrystalline polypropylene films as a function of temperature and orientation by Brillouin scattering, with particular emphasis on the change of elastic constants near the glass transition region. Brillouin light scattering is a new technique for polymer film analysis and is an excellent method to determine the elastic properties of unoriented and oriented films.<sup>9</sup> The polymer sample is not perturbed by external

probes yet fast, accurate measurements with an uncertainty of 1 - 3 percent can be made. The size of the amorphous and crystalline regions of polypropylene are smaller than the wavelength of light associated with Brillouin scattering and the results will reflect contributions from both phases; however, the information obtained should complement those studies made by ultrasonic and dynamic loss measurements.

### Experimental

The preparation of polycrystalline polypropylene film samples suitable for Brillouin scattering has been described previously.<sup>8</sup> Besides an unstretched sample, two film specimens of draw ratios 4.0 and 6.8 are prepared for the temperature dependent study. A water-methanol mixture is used in the flotation method to determine the density of the film samples. The density of the film is not altered by stretching; a value of  $.899 \pm .002 \text{ g/cm}^3$  at 25°C was measured for all film samples.

Brillouin spectra are obtained as follows. Single frequency 4880 Å light from a Spectra Physics model 165 Argon ion laser with an air-spaced etalon is focused on and scattered from the sample. The scattered light is passed through a Burleigh five pass Fabry-Perot interferometer and detected at 90° to the incident radiation with a thermoelectrically cooled photomultiplier tube. The output from the PM tube is fed into a high speed picoammeter and the spectra recorded with an Omnigraphic X-Y recorder. The free spectral ranges used are 33.1 and 31.0 GHz. The magnitude of frequency shift of the acoustic phonon is averaged from two adjacent orders to account for non-linearity of the interferometer.

For measurements made below room temperature, an Air Products Displex refrigerator is used; the Displex uses helium in a closed-cycle cryostat system. The sample compartment is vacuum insulated to prevent frosting of the compartment

windows. A specially designed copper film holder is attached to the copper cold tip of the Displex. The film holder is designed to position the film at  $45^\circ$  with respect to the incident beam. A  $12.2 \times 5.3$  mm hole provides an entry-exit port for the light and is bevelled on one side to allow the laser light to enter without obstruction. The film sample is mounted to the film holder as shown in Fig. 1. A thin copper sheath about .2 mm thick is folded around the film and is sandwiched between the copper holder and an outer copper plate, 1.6 mm thick. For Brillouin spectra recorded at higher than room temperature, the film is again surrounded by a thin copper sheath and attached to a rectangular brass frame. The rectangular frame is inserted through a slot between two copper blocks machined with entry-exit ports. Heating tape surrounds the copper block assembly and the power supplied is controlled by a Variac transformer.

The temperature readings are recorded with a Chromel-Constantan thermocouple attached to the copper plate or sheath as close as is feasible to the scattering center. The accuracy of the low temperature reading is  $\pm .5^\circ\text{C}$ ; for the high temperature readings, the accuracy is  $\pm 2^\circ\text{C}$ .

The density of the polypropylene film at various temperatures is determined with the coefficient of thermal expansion,  $6.8 \times 10^{-5} \text{ K}^{-1}$ . 10

The velocity of an acoustic wave in a solid medium can be calculated from the frequency shift of the scattered light by the following equation:

$$V_s = \frac{f_B \lambda_i}{2n \sin(\theta/2)} \quad (1)$$

where  $f_B$  is the frequency shift (in Hz) of the scattered light,  $\lambda_i$  is the wavelength of the incident radiation,  $n$  is the refractive index of the medium and  $\theta$  is the scattering angle. When the film is oriented  $45^\circ$  with respect to the incoming beam and the scattering angle is equal to  $90^\circ$ , the velocity becomes independent of the

refractive index, and Eq. (1) assumes a simple form:<sup>11</sup>

$$V_s = f_B \lambda_i / \sqrt{2} \quad (2)$$

Equation (2) is very useful as the refractive index does not enter the equation. Thus, hypersonic velocity  $V_s$  can be determined without the need of measuring the refractive index as a function of temperature. The velocity data reported here are determined using Eq. (2).

### Results and Discussion

The hypersonic velocities of the quasi-longitudinal and quasi-transverse phonons were obtained from the Brillouin spectra of isotactic polypropylene film samples of draw ratios (D.R.) 1.0, 4.0, and 6.8. Figure 2 shows the velocity-temperature results for the three polypropylene samples when the film is oriented along the z-direction ( $\alpha=0^\circ$ ,  $\alpha$  being the angle between the scattering vector and the z-axis, the z-axis being taken parallel to the stretch axis). As been noted in earlier studies, the magnitude of the velocity increases with increasing draw ratio, indicative of increasing orientation of the polymer chains along the stretch direction. As can also be seen over the temperature range (150-330 K) studied, the velocities increase as the temperature decreases, except in the region of the glass transition zone. The glass transition zone shows a decrease in velocity for D.R. 1.0 and 6.8 with scatter occurring for the D.R. 4.0 film. Similar results were obtained with the q vector oriented at  $30^\circ$  with respect to the z-axis as shown in Fig. 3 which also includes the quasi-transverse phonons. The lower two curves in Fig. 3 refer to the quasi-transverse phonons and the upper two refer to the quasi-longitudinal phonons. The increase in velocity of the quasi-transverse phonons before and after the glass transition zone is not as large as that for the quasi-longitudinal phonons.



Likewise, when the  $q$  vector is oriented  $90^\circ$  to the  $z$ -direction (or parallel to the  $x$ -axis) scatter occurs in the glass transition zone, as Fig. 4 shows. Noticeable in Fig. 4 is the lack of a large break in slope between the pre- $T_g$  and post- $T_g$  curves, but the effect of the glass transition zone in the temperature range between 250-295 K is clearly evident.

Due to the fact that the Brillouin peak frequency in an amorphous polymer is determined by a large part by the relaxed part of the bulk modulus (i.e. the adiabatic compressibility contribution), the hypersonic frequency (or velocity) versus temperature plot will reflect the effect of the glass transition observed in the thermodynamic measurement which is at very low frequency. For this reason, the glass transition temperature  $T_g$  may be obtained from the velocity-temperature data from the intersection of the pre- $T_g$  and post- $T_g$  curves or from the point of inflection when the curve is gradual or S-shaped. However, our results on the oriented films show that the shape of the velocity versus temperature curves depends on the direction of the  $q$  vector with respect to the  $z$ -axis. Thus, it appears that the glass transition has a complex effect on the oriented polymer solids and careful consideration is needed in their interpretation.

In ref. 6, Wada et. al. have reported the results which suggest two groups of amorphous phases in polycrystalline PP, one of which is composed of atactic chains located in the region between the folded surface of the lamellae (region I). This region has the glass transition and primary relaxation in the lower temperature at about  $-19^\circ\text{C}$  ( $T_{g1}$ ). The other group is composed mainly of isotactic chains and has the transition and relaxation in the higher temperature at about  $16^\circ\text{C}$  ( $T_{g2}$ ). This group is located in the region between lamellae which are oriented in the radial direction (region II). Wada et. al. have provided evidences to show each of these regions to be a class of static rather than a single phase. There does exist the possibility that the glass transitions we have observed do reveal two separate

transitions bordered by  $T_{g1}$  and  $T_{g2}$ . As shown in Fig. 2, a distinct break exists in our velocity-temperature curves at approximately 290 K but due to the sensitivity of the Displex overheating near room temperature, there are a paucity of points near the region. This temperature is close to  $T_{g2}$ . However, the position of the low temperature depends on the stretch ratio as well as on the angle  $\alpha$ . For the unstretched film, the temperature which shows the break in the velocity versus temperature curve occurs at about 260 K, which is slightly higher than the  $T_{g1}$  value at  $-19^\circ\text{C}$ . However, the difference may be due to the lower crystallinity (about 48%) of the present sample, in contrast to the 52% crystallinity of the sample of Wada *et. al.*

The effects of orientation on the glass transition may suggest possible loss of chain orientation. It is known that chain mobility does increase for polymers heated through  $T_g$  as the Brownian motion of the polymer chains increases. This is shown by the decrease in velocity of the acoustic phonons when heated through  $T_g$ . It is also known that highly oriented films generally show a greater resistance to change in chain mobility due to the increased rigidity than do unoriented films. The question arises as to whether the decrease in the sonic velocity observed in our velocity-temperature curves in the glass transition region reflects a loss of orientation.

Considering the behavior of the velocity-temperature change for films stretched to different degrees, this is probably the case. As shown in Fig. 2, the unstretched film (D.R.1) displays a slight minimum in the sonic velocity in the glass transition region, with the lower break temperature designated as  $T_{g1}$  located at about 260 K. However,  $T_{g1}$  for the highly drawn (D.R. 6.8) films shifts 30 K to about 230 K.  $T_{g1}$  for the D.R. 4.0 film lies in between. This behavior is expected for orientation of the amorphous chains when subjected to high constraint by surrounding crystallites. The different  $T_{g1}$  positions as shown in Figs. 3 and 4 for  $\alpha = 30^\circ$  and  $90^\circ$  indicate that for a stretched film, the amorphous chains are oriented anisotropically. For the

film at a given draw ratio, chains oriented along the stretched axis have the capability of giving rise to the maximum lowering of  $T_{g1}$ .

Additional insight of orientational effects and the glass transition was obtained from a determination of the elastic constants  $C_{33}$ ,  $C_{11}$ ,  $C_{44}$ , and  $C_{13}$  as a function of temperature. The elastic constants are calculated from the quasi-longitudinal and quasi-transverse phonon velocities measured at  $0^\circ$ ,  $30^\circ$ , and  $90^\circ$  angular positions of the film and the Cristoffel equation<sup>13</sup> using the method given in ref.12. The Cristoffel equation is incorporated into a least squares fitting routine with the best fit of the experimental data providing the four elastic constants.

From the least squares fit, the elastic constants as a function of temperature for D.R.1 are plotted in Fig. 5. For isotropic materials,  $C_{33} = C_{11}$ .  $C_{44}$  is associated with the shear or transverse phonon and shows a gradual increase as temperature is decreased, while  $C_{13}$  remains essentially unchanged. Both  $C_{44}$  and  $C_{13}$  are theoretically calculated elastic constants from the least squares fit since no transverse wave is observed in the Brillouin spectra of unoriented films. The accuracy of the  $C_{44}$  and  $C_{13}$  data in the unoriented film is uncertain at present. Note the anomaly in the  $C_{33}$  (or  $C_{11}$ ) data near the glass transition region.

The temperature dependence of the elastic constants for an oriented film, D.R.4 are shown in Fig. 6. In this case, the film becomes anisotropic and  $C_{33}$  and  $C_{11}$  are no longer equal, yet  $C_{33}$  behaves similar to its counterpart in the unoriented film, and clearly indicating of the increasing orientation along the stretch direction. It is particularly interesting that  $C_{44}$  does not increase as it did (theoretically) in the unoriented film, and appears to decrease very slightly as lower temperatures are approached. The  $C_{11}$ ,  $C_{33}$ , and  $C_{44}$  data show anomaly in the glass transition region, with the  $C_{33}$  result displaying the largest effect.  $C_{13}$  is again unaffected by temperature. For the highly oriented film, D.R.6.8, shown in Fig. 7, a significant dip at approximately 270 K is seen with  $C_{33}$ .  $C_{44}$  and  $C_{13}$  remain essentially constant while  $C_{11}$  increases gradually as it did in Fig. 6.  $C_{11}$  also shows scatter in the

glass transition region, but the effect is less pronounced than that displayed by  $C_{33}$ .

From the elastic constant data, it is clear that the glass transition has a most significant effect on the elastic constant  $C_{33}$ , although the effect on  $C_{11}$  and  $C_{44}$  is not negligible. In view of the two amorphous regions model of Wada *et. al.* it is reasonable to expect that at room temperature, chains in region I in the rubber state undergo segmental motion. Decreasing the temperature of the films below room temperature would force the chains in region I, which have already been oriented along the z-axis due to stretching, into a more ordered state. This should affect  $C_{33}$  very pronouncedly. Thus, the sonic data which show lowering of  $T_{g1}$  with increasing draw ratio are presumably associated with the orientation of the chains in the amorphous region I. The effect on the amorphous chain in region II by stretching is not expected to be significant because chains in this region are frozen in the glass state. According to Wada *et. al.*<sup>6</sup>, region I is rich in atactic chains with a small fraction of isotactic chains serving as loose loop chains and tie molecules connecting the lamellae. Thus, by orienting the amorphous chains along the stretch axis, the chains are forced into a more strained state. As a result, the temperature will have a significant effect on  $C_{33}$ , particularly in the glass transition region.

Ultrasonic measurements have been made on extruded polypropylene rods between 190 and 270 K by the workers listed in ref. 14. As a means of comparison, Figure 8 shows the results we obtain for  $C_{33}$  and  $C_{11}$  at 190 K as a function of draw ratio for polypropylene film with the ultrasonic results of extruded rods at 190 K reported in ref. 14. Included for comparison, there is a fairly large discrepancy between the  $C_{33}$  and to a lesser extent between the  $C_{11}$  elastic constants. Previous investigations have shown that at room temperature,  $C_{33}$  obtained by Brillouin scattering for both drawn polypropylene film and extruded rods is slightly greater in the film samples.<sup>8,15</sup>  $C_{11}$ , however, shows a slightly greater magnitude for the extruded samples than for the drawn films. Figure 8 shows opposite behavior for  $C_{11}$  with the ultrasonic values lower in magnitude than for the drawn films. Thus, there is a

substantial difference between the Brillouin and ultrasonic data for both  $C_{33}$  and  $C_{11}$ . Also shown in Fig. 8 are the theoretically calculated curves for  $C_{33}$  and  $C_{11}$  designated as "Voigt" which were taken from Fig. 4(a) of ref. 14. The Voigt model represents a pseudo-affine deformation scheme to model the effect of the drawing on the elastic constants by taking the ensemble average of the elastic constants of basic transversely isotropic microscopic units.<sup>16</sup> This model is similar to the orientational model of Wang and Cavanaugh,<sup>15,17</sup> with the exception that in refs. 15 and 17 the ensemble average of orientation of the basic units is formulated in terms of the

orientation parameters  $\langle P_2(\cos\theta) \rangle$  and  $\langle P_4(\cos\theta) \rangle$ , whereas in ref. 16, the ensemble average is carried out with respect to the deformed state and approximation made to connect the effect of orientation to the draw ratio. Since the draw ratio is not related to the orientation parameters in a simple way, the Voigt model of ref. 16 will not correctly account for the effect of deformation on the elastic constants even if the orientation of the polymers does occur affinely. The solid curves marked as "orientation" refer to the elastic constants calculated according to the method recently developed by Cavanaugh and Wang.<sup>17</sup> This method uses two parameters which relate the intrinsic elastic constants of perfectly oriented sample  $C_{11}^\circ$  and  $C_{33}^\circ$  to the elastic constants  $C_{11}$  and  $C_{33}$  at a given orientation. The method also uses the assumption that  $C_{44}^\circ = C_{44}$ , but this is supported by the experimental result as  $C_{44}$  of the PP film remains unchanged by stretching. Using a least squares program and equations developed in ref. 17, we have determined the intrinsic elastic constants along with the orientation parameters  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  from the experimentally determined elastic constants. The determined orientation parameters and intrinsic constants are then used to predict the elastic constants as a function of draw ratio. The results are shown in Fig. 8. The values of intrinsic elastic constants and  $\langle P_2 \rangle$  are given in Table I. One notes that both  $C_{33}$  and  $C_{11}$  calculated from the orientation model agree quite well the experimental values at 190 K. The Voigt model prediction gives results slightly lower than the experimental values. The agreement of the orientation model

with the experimental results suggests that stretching of PP induces chains in the lamellae to orient in a direction perpendicular to the stretch direction and the amorphous chains to orient in the stretch direction. However, both the Voigt and the orientation models do not agree with the ultrasonic data.

Besides the discrepancy between the  $C_{33}$  and  $C_{11}$  elastic constants of Brillouin and ultrasonic results, there is also a large difference observed from the  $C_{13}$  elastic constant. In ref. 17, it is shown that results upon drawing the changes of  $C_{13}$  as determined by Brillouin scattering are quite similar in the extruded rod and the oriented film. The present  $C_{13}$  value at 190 K is equal to  $3.4 \times 10^{10}$  dyn/cm<sup>2</sup> for the D.R. 6.8 film and equal to  $3.5 \times 10^{10}$  dyn/cm<sup>2</sup> for the D.R. 4.0 film. These values contrast with the ultrasonic value of  $1.5 \times 10^{10}$  dyn/cm<sup>2</sup> at the draw ratios of 4.0 and 6.8.<sup>14</sup> The discrepancy between the ultrasonic and Brillouin scattering results is very significant. It is not clear that the difference in the two results is a manifestation of considerable dispersion in the PP films or that the ultrasonic data are in error. It is hoped that further experiments carried out using ultrasound and Brillouin scattering at different scattering angles will clarify this discrepancy.

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### Figure Captions

- Figure 1. Film holder apparatus. A-outer copper plate; B-thin sheath surrounding film sample; C-machined film holder which attaches to the cold tip of the cryostat. All components are copper. Arrows indicate this direction of incident and scattered radiation.
- Figure 2. Longitudinal phonon velocities as a function of temperature and draw ratio.  $\alpha$  equals  $0^\circ$ . 2% error bars are shown.  $\bullet$  - cooling sample;  $\blacksquare$  - heating sample.
- Figure 3. Quasitransverse,  $\circ$ , and quasilongitudinal,  $\bullet$ , phonon velocities as a function of temperature and draw ratio.  $\alpha$  equals  $30^\circ$ . 2% error bars are shown.  $\circ, \bullet$  - cooling sample;  $\square, \blacksquare$  - heating sample.
- Figure 4. Longitudinal phonon velocities versus temperature and draw ratio.  $\alpha$  equals  $90^\circ$ . 2% error bars are shown.  $\bullet$  - cooling sample;  $\blacksquare$  - heating sample.
- Figure 5. Elastic constants as a function of temperature for D.R. 1.  $\Delta$  -  $C_{33}(=C_{11})$ ;  $\blacksquare$  -  $C_{44}$ ;  $\bullet$  -  $C_{13}$ . Solid points are theoretically calculated values.
- Figure 6. Elastic constants as a function of temperature for D.R. 4.  $\Delta$  -  $C_{33}$ ;  $\circ$  -  $C_{11}$ ;  $\hexagon$  -  $C_{13}$ ;  $\square$  -  $C_{44}$ .
- Figure 7. Elastic constants as a function of temperature for D.R. 6.8.  $\Delta$  -  $C_{33}$ ;  $\circ$  -  $C_{11}$ ;  $\hexagon$  -  $C_{13}$ ;  $\square$  -  $C_{44}$ .
- Figure 8. Comparison of  $C_{33}$  -  $\bullet$  and  $C_{11}$  -  $\blacksquare$  obtained Brillouin scattering with the ultrasonic results  $\circ, \square$  at 190 K. Also shown are the elastic constants calculated by the orientation and Voigt models.



Table I

Intrinsic Elastic Constants and the Orientation Parameters of Isotactic Polypropylene  
Films for those Films with  $R_s = 1.0, 4.0$  and  $6.8$ .

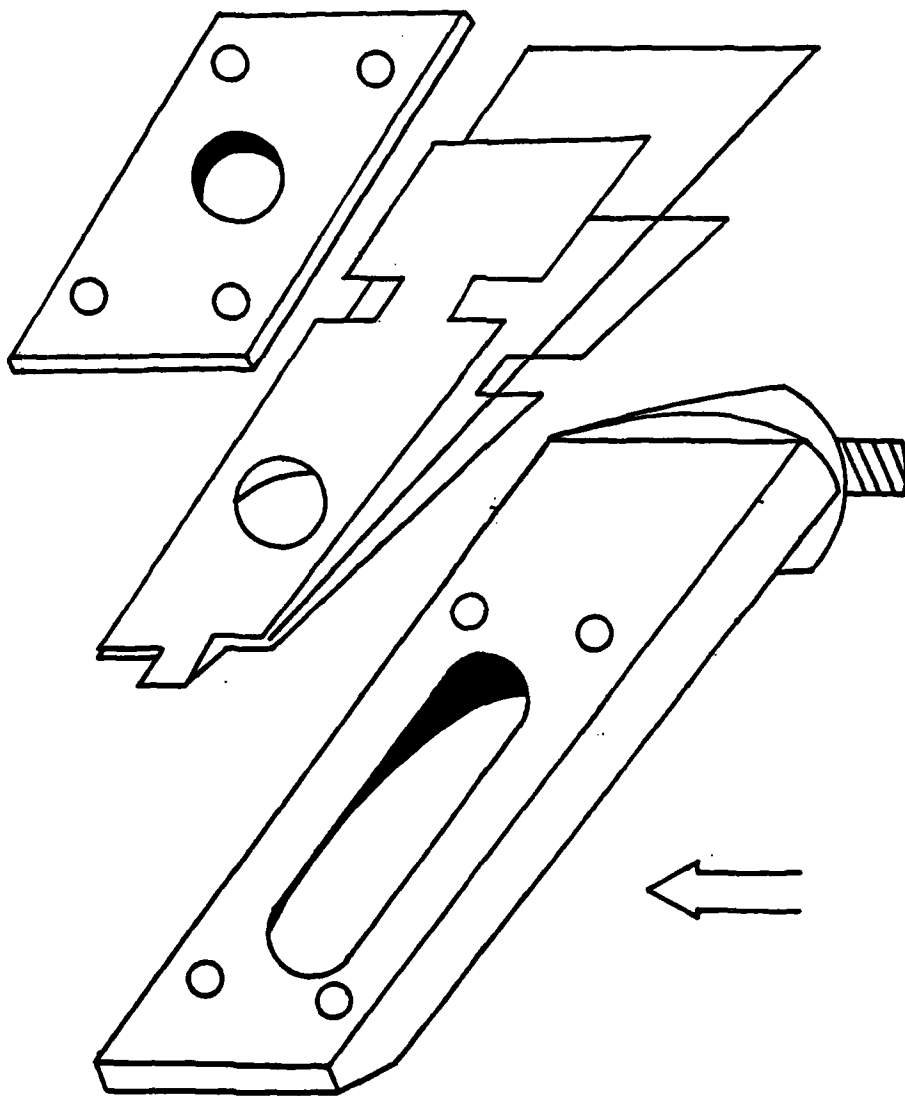
| Intrinsic Elastic Constants in<br>units of $10^{10}$ dyn/cm <sup>2</sup> |                              |                              |                              | Orientation Parameters<br><P <sub>2</sub> > |                     |                     |
|--|------------------------------|------------------------------|------------------------------|---|---------------------|---------------------|
| C <sub>11</sub> <sup>°</sup>   | C <sub>33</sub> <sup>°</sup> | C <sub>44</sub> <sup>°</sup> | C <sub>13</sub> <sup>°</sup> | R <sub>s</sub> =1                           | R <sub>s</sub> =4.0 | R <sub>s</sub> =6.8 |
| 3.25   | 20.23                        | 1.65                         | 0.34                         | 0.0   | 0.53                | 0.67                |

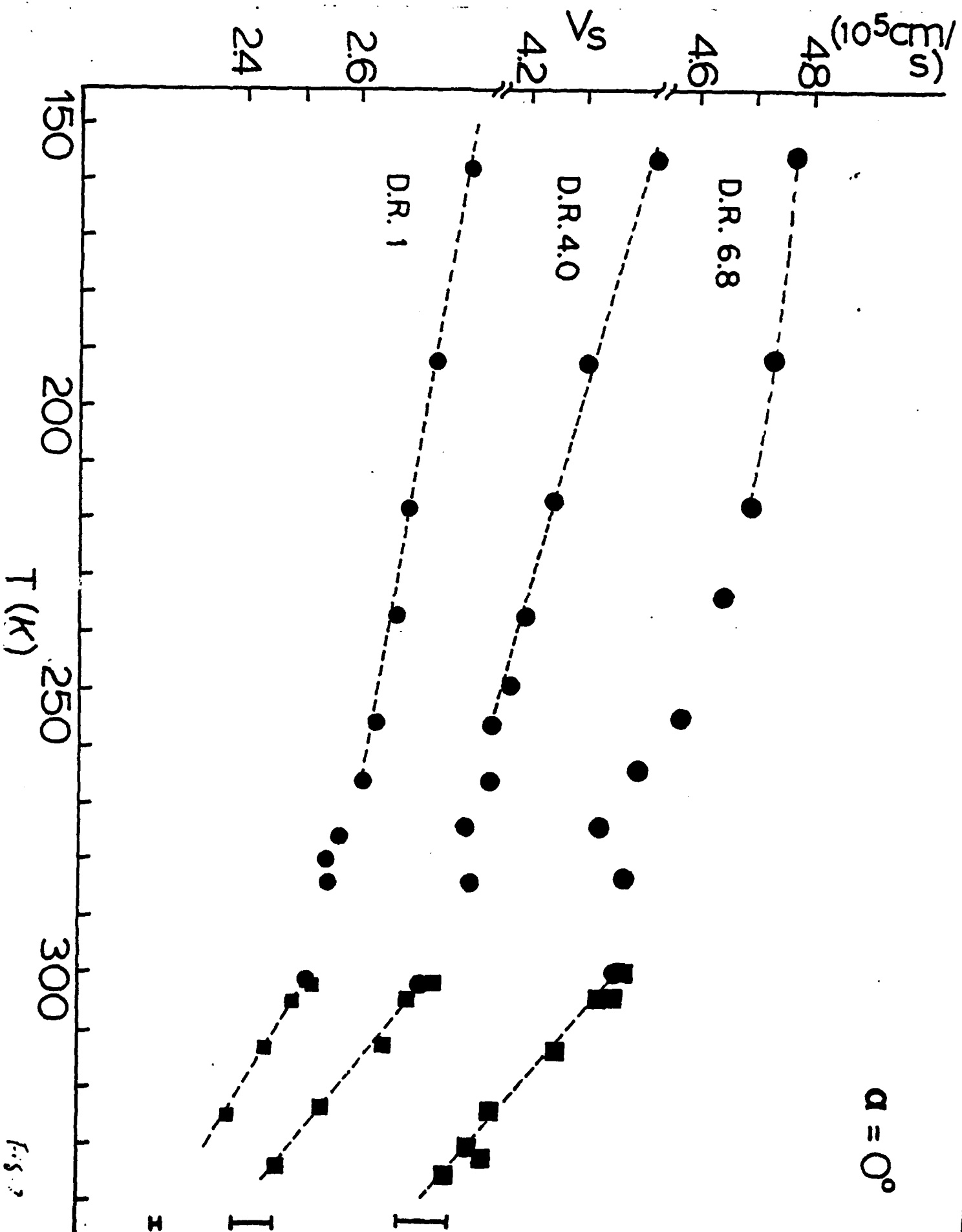


A

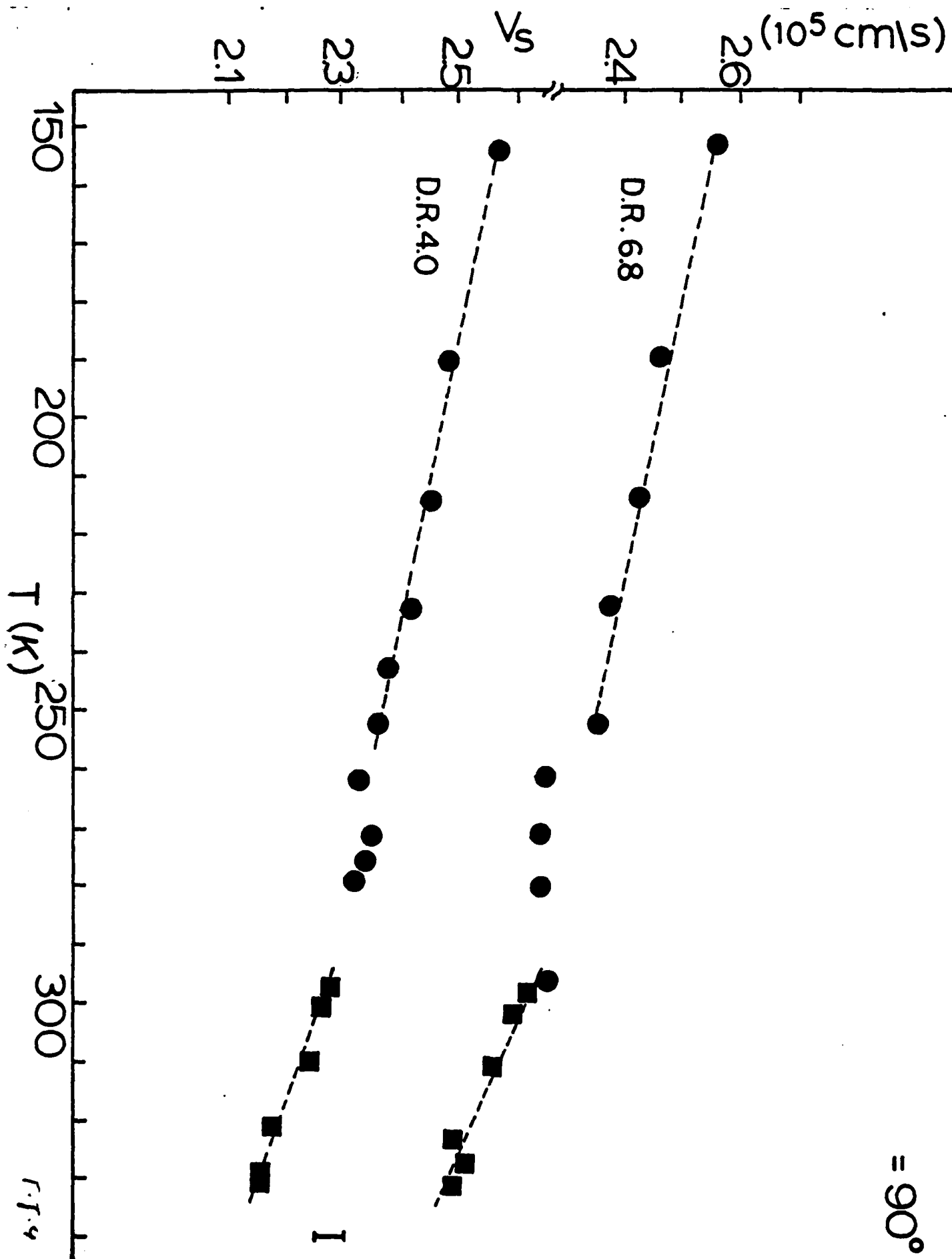
B

C

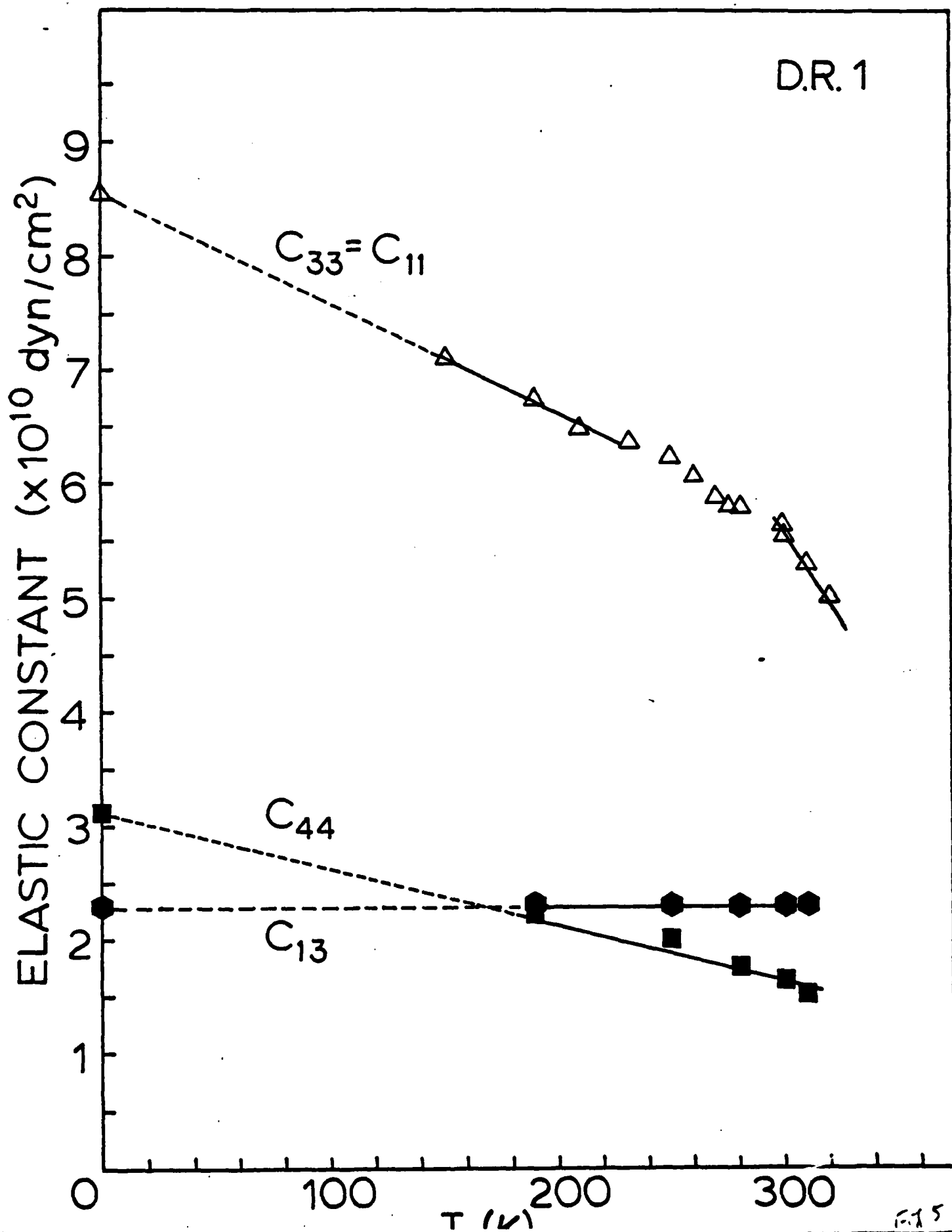




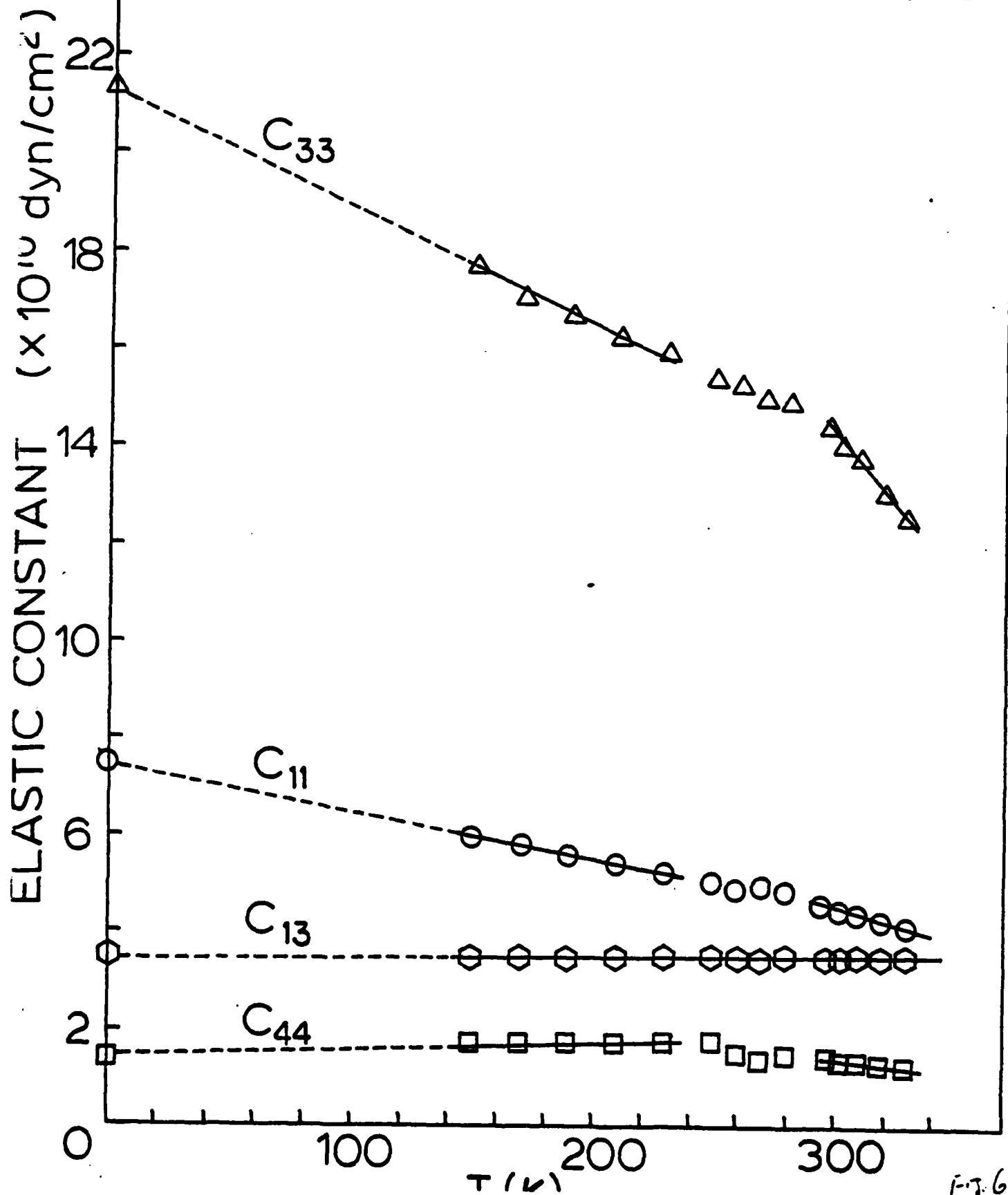




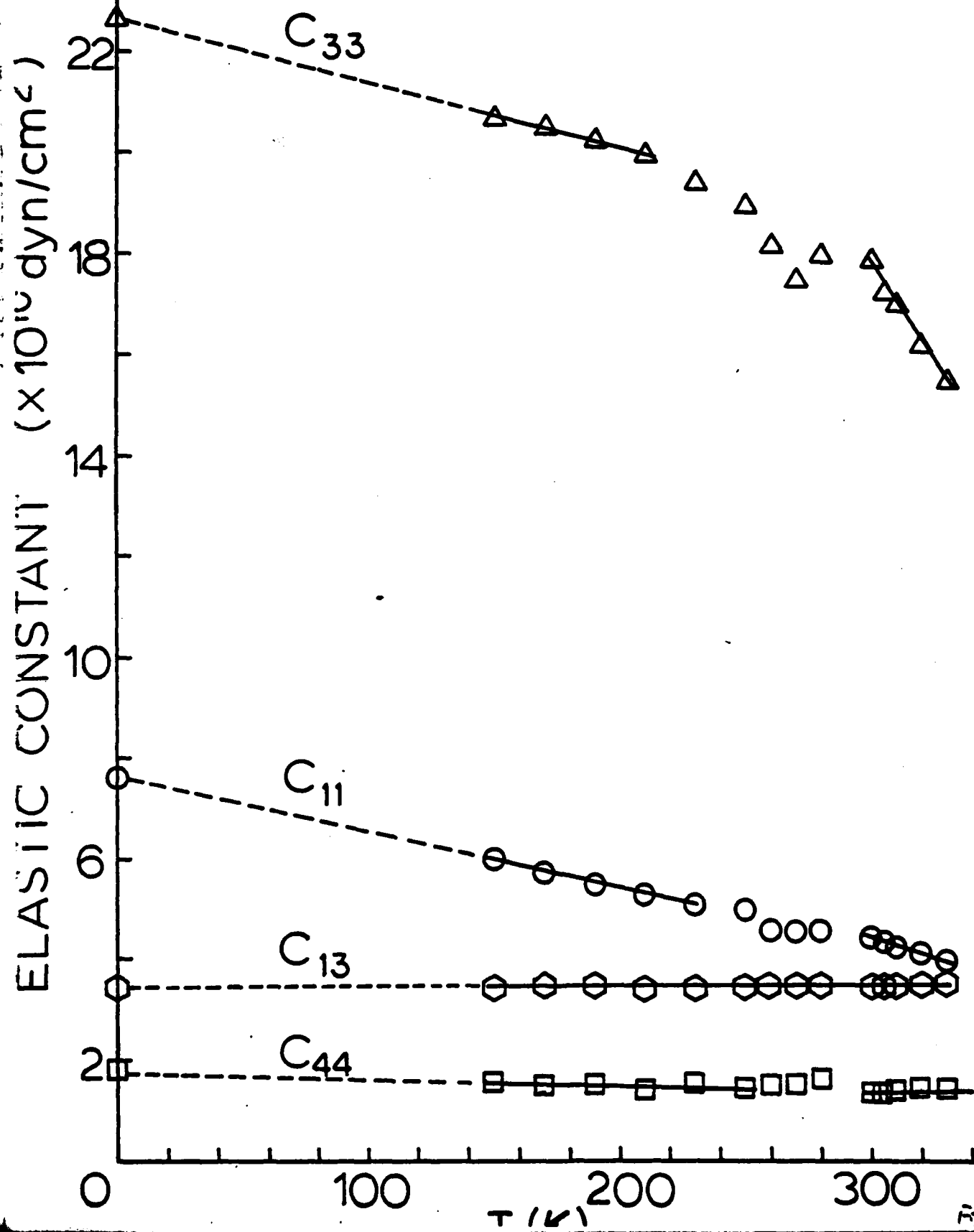
D.R. 1



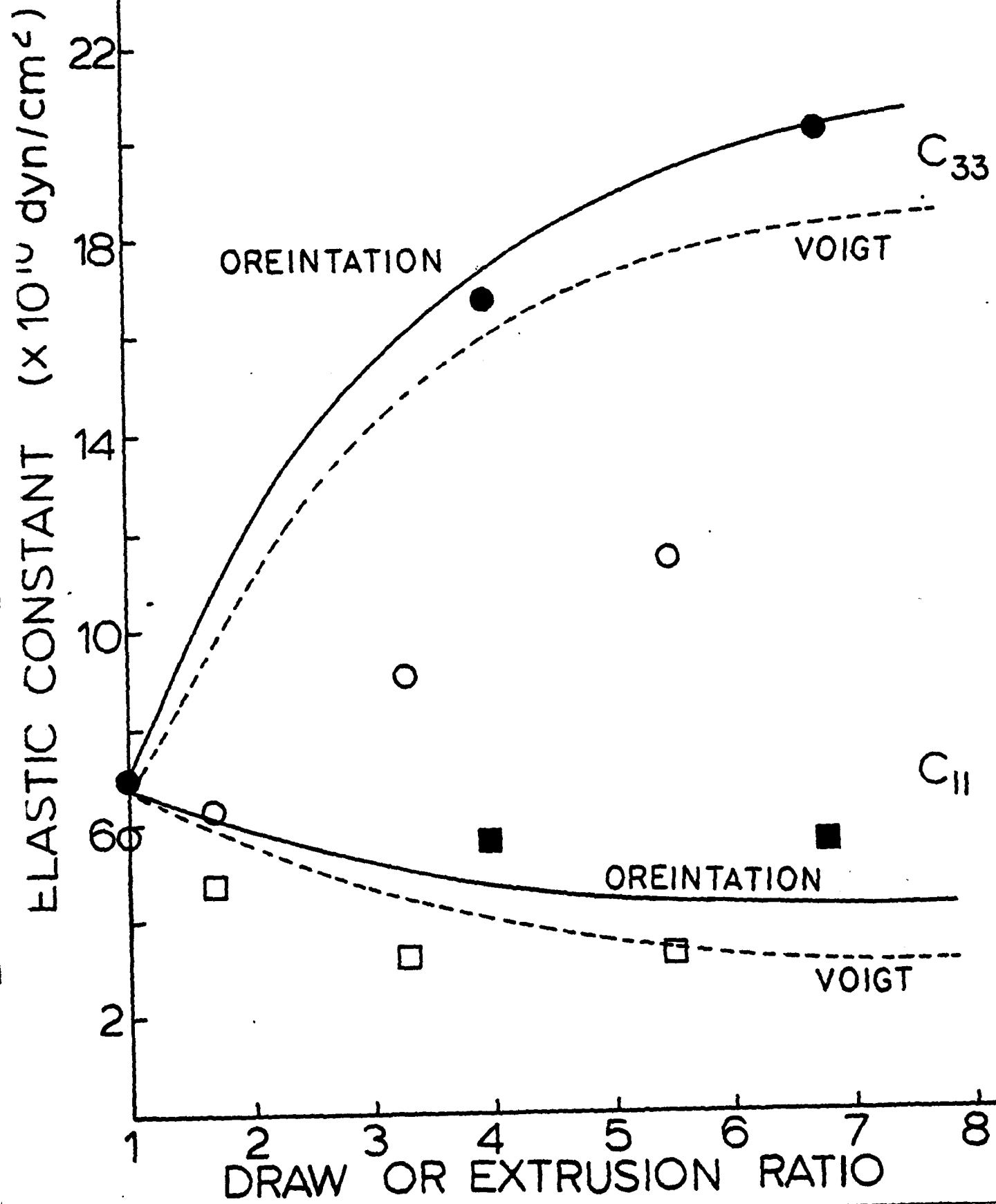
D.R.4.0



D.R.6.8







**DAT**  
**ILM**